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(54) Title: COMPOSITE MATERIAL AND PRODUCTION OF THE COMPOSITE MATERIAL, AND COMPOSITE-MATERIAL-CONTAINING RESIN COMPOSITION AND PRODUCTION OF THE RESIN COMPOSITION		
(57) Abstract <p>A composite material of layered silicate and organic polymer, (as shown in the figure wherein (1) is layered silicate and (2) is ionomer) having heat stability, and containing silicate layers that are not parallel and between which the distance is increased; a production method for a composite material utilizing no polymerization but dispersion of layered silicate in organic polymer materials other than amide; a composite-material-containing resin composition containing the composite material; and a production method for the resin composition, are provided. Particularly, a composite material is made by dispersing, mixing, drying, and crushing 100 parts by weight ionomer made of ethylene methacrylate copolymer that is partially or entirely neutralized by alkali metal or alkaline-earth metal with at least 0.05 parts by weight of layered silicate in water to introduce the ionomer into a layered silicate of the silicate layers.</p> <div style="text-align: center;"> </div>		

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TITLE

COMPOSITE MATERIAL AND PRODUCTION OF THE COMPOSITE MATERIAL, AND COMPOSITE-MATERIAL-CONTAINING RESIN COMPOSITION AND PRODUCTION OF THE RESIN COMPOSITION

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This patent application claims priority to Japanese Patent Application Nos. 8-65355 and 8-302368, which is incorporated herein by reference.

Field of the Invention

10 The present invention is concerned with both a composite material used for mixing with an organic polymer material to improve mechanical properties, gas barrier properties, heat resistance, or transparency of the organic polymer material, and production of the composite material. In detail, the present invention is concerned with both a composite material containing silicate layers
15 between which an ionomer is introduced, and production of the composite material. The present invention is also concerned with a composite-material-containing resin composition containing both an organic polymer material compatible to the ionomer and produced composite material, and production of the resin composition.

20

Background

Development of a composite material containing silicate layers between which an ionomer was introduced was attempted, and is described in Chuzo Kato (Polymer, 1970, Vol. 19, No. 222, pp. 758-764) and Chuzo Kato and Kazuyuki
25 Kuroda (Clay Science, 1986, Vol. 26, No. 4, pp. 292-305). However, it was difficult to introduce an organic polymer material to a silicate layer in order to increase the distance between the layers, and to make the layers unparallel with each other to disperse clay minerals.

Clay mineral/polyamide resin compositions characterized by, if necessary,
30 treating silicate layers that make up swelling clay minerals with an alkylamine swelling agent, then impregnating and polymerizing the monomers, were

developed (Japanese Kokai Patent Application Nos. Sho 58[1983]-35211 and Sho 58[1983]-35542) as composite materials in order to solve the problems.

A composite material made by mixing resin that contained the polyamide with silicate layers making up the layered silicate and having both thickness of 7-12 Å (angstrom) and a distance between the layers of 30 Å or more, then ion-bonding a part of a polyamide polymer chain to the silicate layers, was reported as a composite material made by ion-bonding a part of the polyamide polymer chain to the silicate layers (Japanese Kokai Patent Application No. Sho 62[1987]-74957).

A production method for the composite material employed in the following processes, i.e., a contact process in which layered silicate was brought into contact with a swelling agent to make a composite that was swollen by polyamide contained in the monomer; a mixing process in which the produced composite was mixed with polyamide monomer; and polymerization process in which the mixture was heated to the required temperature to carry out polymerization (Japanese Kokai Patent Application No. Sho 62[1987]-74957). Because the production process contained a polymerization process it was not necessarily easy to make composite materials, and it was difficult to apply it to other than the polyamide.

A composite-material-containing resin composition having a distance between the layers of 30 Å or more, making the layers unparallel to each other, and made by compounding polyamide with a layered silicate/alkylamine swelling agent composite material made by dispersing both layered silicate and an alkylamine swelling agent in water, then drying, was reported (U.S. Patent No. 5,385,776). However, because an alkylamine swelling agent having a low molecular weight was contained in the final products, poor thermal stability was obtained. Because increasing the distance between the layers 30 Å or more makes the layers unparallel to each other, it was difficult to make a composite-material-containing resin composition having improved dispersibility.

Problems to be solved by the invention

Development of production methods for a composite material involving no polymerization process and using organic polymer materials other than polyamide which can disperse layered silicate was desired.

5 The purpose of the present invention is to provide a composite material consisting of both layered silicate and an organic polymer material, having thermal stability, containing silicate layers between which the distance is increased or which are not parallel each other, and to provide a production method for a good composite material which is easy and requires neither a process in
10 which layered silicate is brought into contact with an alkylamine swelling agent or in which polymerization is carried out when a composite material having improved dispersibility either to increase the distance between the silicate layers or to make the layers be unparallel each other is made.

 The purpose of the present invention is to provide both a
15 composite-material-containing resin composition that contains the composite materials and a production method for the composition.

 In detail, the purpose of the present invention is to provide a composite material consisting of both an ethylene ionomer and layered silicate, and production of the composite material, and a composite-material-containing resin
20 composition that contains the composite material, and production of the composition.

Summary of Invention

 Research was undertaken by the inventors to solve the problems, and it
25 was found that a composite material of both layered silicate and an organic polymer material, made with a process involving no polymerization, able to be used for various types of resin, having improved dispersibility that either increases the distance between silicate layers or makes the layers unparallel to each other, could be made in a simple production process by selecting both organic polymer
30 material (A), satisfying specific conditions as an organic polymer material making up a composite material with layered silicate, and organic polymer material (B), which is kneaded with the composite material, and a production method for a

composite-material-containing resin composition that contains the composite material.

Therefore, a production method for a composite material is characterized by dispersing, mixing, drying, and crushing a polar organic polymer that is either
5 soluble or dispersible in water, and fusible with silicate layers in a polar solvent, to introduce the above-mentioned polar organic polymer to a layered silicate of the above-mentioned silicate layer.

A production method for a composite material also is characterized by using an ionomer as the above-mentioned polar organic polymer.

10 A production method for a composite material also is characterized by dispersing, mixing, drying, and crushing 100 parts by weight potassium ionomer made of potassium in which ethylene methacrylate copolymer is either partially or entirely neutralized, with 0.5-300 parts by weight silicate layers in water, to introduce potassium ionomer to a layered silicate of the above-mentioned silicate
15 layers.

A composite material is characterized by dispersing, mixing, drying, and crushing 100 parts by weight sodium ionomer that is made of ethylene methacrylate copolymer which is either partially or entirely neutralized with sodium and that can be soluble or dispersible in water, with 0.5-300 parts by
20 weight silicate layers in water to introduce sodium ionomer to a layered silicate of the above-mentioned silicate layers.

A composite material also is characterized by containing both a polar organic polymer that is either soluble or dispersible in water and fusible, and that is introduced between the above-mentioned silicate layers.

25 A composite material also is characterized by compounding composite materials made by a production method described in any of Claims 1-4, composite materials described in Claim 5, and an organic polymer material compatible to the above-mentioned polar organic polymer to disperse and pack 0.05 part by weight or more of the above-mentioned silicate layers in 100 parts by weight of a mixture
30 of the above-mentioned polar organic polymer and the above-mentioned organic polymer material.

A composite-material-containing resin composition is characterized by containing a melted and kneaded material comprising composite materials made by one of the production methods described in Claims 1-4, or composite materials described in Claim 5, and an organic polymer material compatible with the
5 above-mentioned polar organic polymer, and by containing both the above-mentioned polar organic polymer and 0.05 part by weight or more of the above-mentioned silicate layers to 100 parts by weight of the above-mentioned organic polymer material.

10 **Brief Description of Figures**

Figure 1 explains the presence of both the layered silicate (1) and the ionomer (2) in each composite material made in Application Examples 1-3 of the present invention.

Figure 2 explains the presence of both the layered silicate (1) and the
15 ionomer (2) in each composite material made in Comparative Examples 1-4 of the present invention.

Figure 3 shows an optical microscopic photograph of a composite material made in Application Example 4 of the present invention. (A) is a photograph with a magnification of 15 times. (B) is a photograph with a magnification of 40 times.

20 Figure 4 shows an optical microscopic photograph of a composite material made in Application Example 5 of the present invention. (A) is a photograph with a magnification of 15 times. (B) is a photograph with a magnification of 40 times.

Figure 5 shows an optical microscopic photograph of a composite material made in Application Example 6 of the present invention. (A) is a photograph with
25 a magnification of 15 times. (B) is a photograph with a magnification of 40 times.

Figure 6 shows a transmission electromicrograph photograph of a composite material made in Application Example 6 of the present invention (magnification: about 70,000 times)

Figure 7 shows an optical microscopic photograph of a composite material
30 made in Comparative Example 5 of the present invention. (A) is a photograph with magnification of 15 times. (B) is a photograph with a magnification of 40 times.

Figure 8 shows a transmission electromicrograph of a composite material made in Application Example 7 of the present invention (magnification: about 100 times).

Figure 9 shows a transmission electromicrograph of a composite material made in Comparative Example 6 of the present invention (magnification: about 100 times).

Application of the invention

Specific conditions of organic polymer material (A) include being soluble or dispersible in water and being fusible. An organic polymer material able to form a composite material containing organic polymer material (A), which is introduced between the silicate layers by mixing and dispersing either an aqueous solution or an aqueous dispersion of organic polymer material (A) with an aqueous silicate dispersion made by dispersing layered silicate in water, followed by drying then crushing the mixture, must be chosen.

Detailed examples of organic polymer material (A) include ionomers made by partially or entirely neutralizing methacrylic acid in a random copolymer of ethylene and methacrylic acid with an alkali metal or alkaline-earth metal. Because potassium has good dispersibility in water, it is especially suitable. However, other metals typically used in making ionomers, including metals such as sodium or magnesium, which are either dispersible or soluble in water, can be used.

A composite material containing an ionomer that is introduced between the silicate layers making up the layered silicate can be made by mixing an aqueous silicate dispersion, made by dispersing 0.5-300 parts by weight layered silicate in water with an aqueous polymer dispersion made by dispersing 100 parts by weight ionomer in water, drying, and crushing the mixture. It can be verified by both the peak position and intensity measured by wide-angled X-rays that the produced composite material contains ionomer introduced between the silicate layers.

Organic polymer material (B) kneaded with a composite material must be compatible with organic polymer material (A), and must be able to be melted and kneaded. Compatibility means either complete compatibility or good affinity at

the interface. If there is no compatibility, it is difficult to disperse silicate layers of layered silicate in a final material during the kneading process.

Examples of organic polymer material (B) include random copolymers of ethylene and methacrylic acid; ionomers of random copolymer of ethylene and
5 methacrylic acid partially or entirely neutralized particularly with metals such as sodium, magnesium or zinc; polyesters such as polybutylene terephthalate or polyethylene terephthalate; and polyamides such as nylon 6 or nylon 66. In the case of using an ethylene ionomer, the problem of transparency of the ethylene ionomer being damaged, can be solved by adding an inorganic filler to the
10 ethylene ionomer while at the same time improving the mechanical properties.

Layered silicate should be dispersed and filled in amounts of 0.05 parts by weight or more in 100 parts by weight of a combination of organic polymer materials (A) and (B). When there is less than 0.05 part by weight, unsatisfactory effects result from the filling. When there are more than 300 parts by weight to
15 100 parts by weight of a combination of organic polymer materials (A) and (B), poor dispersion results.

A silicate layer of layered silicate used for the present invention has a thickness of 7-15 Å, and is formed with magnesium silicate or aluminum silicate. Examples include smectite clay minerals such as montmorillonite, saponite,
20 beidellite, nontronite, hectorite, or stevensite, vermiculite, halloysite, and mica. They can be either natural or synthetic. Swelling fluorine mica can be included in the examples. Smectite layered silicate is especially suitable.

Any conventional method may be used for stirring, drying, and crushing, which are carried out in the production method for a composite material of the
25 present invention. Any conventional method may be used for compounding a composite material with organic polymer material (B). However, it is desired to use a kneader having a strong compounding power for transmitting mechanical dispersibility to a composite material and which results in better dispersion of layered silica when organic polymer material (A) has good compatibility to
30 organic polymer material (B). Either a biaxial kneader (rotation in the same direction or in the different direction) or a Yabusu kneader is suitable.

Whether the distance between silicate layers is increased in a composite-material-containing resin composition or whether a composite material having improved dispersibility effective for making the layers unparallel to each other is formed or not is decided by visual observation of the transparency using an optical microscope and by observation using a transmission electron microscope if necessary.

Examples

The present invention is explained with application examples. However, the present invention is not specifically limited by said application examples.

Application Example 1

Powder montmorillonite (Kunipia® F made by Kunimine Kogyo K.K.) (1.0 g) was added to water (100 g); then, the mixture was stirred for about 3 hours to make an aqueous silicate dispersion. Aqueous poly(ethylene-methacrylic acid) potassium salt (MKD100 made by Du Pont-Mitsui Polychemicals Co., Ltd.) dispersion was diluted to disperse the poly(ethylene-methacrylic acid) potassium salt (1.0 g) in water (100 g), then stirred for about 1 hour to make an aqueous polymer dispersion. The produced aqueous polymer dispersion was slowly mixed with an aqueous silicate dispersion, then stirred for about 2 hours. Then, the mixture was completely dried in a pan on a hot plate at about 150°C to make a composite material consisting of layered silicate to polymer with combination ratio of 1:1. The produced composite material was crushed in a mortar.

Application Example 2

Synthetic smectite powder (Smecton® SA made by Kunimine Kogyo K.K.) (1.0 g) was added to water (100 g), then stirred for about 3 hours to make an aqueous silicate dispersion. Aqueous poly(ethylene-methacrylic acid) potassium salt (MKD100 made by Du Pont-Mitsui Polychemicals Co., Ltd.) dispersion was diluted to disperse the poly(ethylene-methacrylic acid) potassium salt (1.0 g) in water (100 g), then stirred for about 1 hour to make an aqueous polymer dispersion. The produced aqueous polymer dispersion was slowly mixed with the

aqueous silicate dispersion: then, the mixture was stirred for about 2 hours. Then, the mixture was dried in a pan on a hot plate at 150°C to make a composite material of layered silicate and polymer with a combination ratio of 1:1. The produced composite material was crushed in a mortar.

5

Comparative Example 1

The same process used in Application Example 1 was used to make a composite material of Kunipia® F made by Kunimine Kogyo K.K. and sodium polyacrylate in a 1:1 ratio.

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Comparative Example 2

The same process used in Application Example 2 was used to make a composite material of Smecton® SA made by Kunimine Kogyo K.K. and sodium polyacrylate in a 1:1 ratio.

15

Comparative Example 3

The same process used in Application Example 1 was used to make a composite material of Kunipia® F made by Kunimine Kogyo K.K. and polyethylene imine in a 1:1 ratio.

20

Comparative Example 4

The same process used in Application Example 2 was used to make a composite material of Smecton® SA made by Kunimine Kogyo K.K. and polyethylene imine in a 1:1 ratio.

25

Application Example 3

Montmorillonite powder (Kunipia® F made by Kunimine Kogyo K.K.) (1.0 g) was added to water (100 g); then, the mixture was stirred for about 3 hours to make an aqueous silicate dispersion. Aqueous poly(ethylene-methacrylic acid) sodium salt (Chemiparl® S-100 made by Mitsui Petrochemical Industries, Ltd.) dispersion was diluted to disperse poly(ethylene-methacrylic acid) sodium salt (3.0 g) in water (100 g), then stirred for about 1 hour to make an aqueous polymer

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dispersion. The produced aqueous polymer dispersion was slowly mixed with the aqueous silicate dispersion, then stirred for about 2 hours. Then, the mixture was completely dried in a pan on a hot plate at about 150°C to make a composite material consisting of layered silicate to polymer with the combination ratio of 1:3. The produced composite material was crushed in a mortar.

X-ray analysis

X-ray analysis was carried out for the produced composite materials. Results are shown in Table I.

10

Table I

Sample	Peak position	Peak intensity
Powder Kunipia® F only	7.4	5000
Powder Smecton® SA only	7.5	4000
Application Example 1	Unable to detect	
Application Example 2	Unable to detect	
Comparative Example 1	7.0	5000
Comparative Example 2	8.0	1500
Comparative Example 3	6.8	2000
Comparative Example 4	6.5	1500
Application Example 3	Unable to detect	

Note: unable to detect = peak intensity of less than 1000 cps

As seen in Table I, peaks (1000 cps or more) were not observed at 2θ up to 10°. So, it is verified that either potassium salt or sodium salt of poly(ethylene-methacrylic acid) was introduced between the silicate layers of the layered silicate to make the silicate layers unparallel to each other, so that the silicate layers could be dispersed. Because peaks of the composite materials made in Comparative Examples 1 and 2 had both the same position and intensity as those of peaks of either Kunipia® F or Smecton® SA powder, neither sodium polyacrylate nor polyethylene imine was introduced between the silicate layers. Both Figures 1 and 2 show the structures. In Figures 1 and 2, 1 represents a

20

silicate layer of layered silicate, and 2 represents an ionomer. In Figure 1, which shows the shape of each composite material made in Application Examples 1-3, silicate layers 1 are not parallel to each other, and ionomer 2 is introduced between the silicate layers extended in the various directions. In Figure 2, which shows the shape of each composite material made in Comparative Examples 1-4, silicate layers 1 are parallel, the distance between the layers is not increased, and ionomer 2 is not introduced between the layers nor present in the outside of the layered silicate particles.

10 Application Example 4

The same method used in Application Example 1 was used to make a Kunipia® F/poly(ethylene-methacrylic acid) potassium salt powder composite material (weight ratio: 1/1) (80 g). The material was dry-blended with pellets of poly(ethylene-methacrylic acid) zinc salt (Himilan® 1706 made by Du Pont-Mitsui Polychemicals Co., Ltd.) (920 g); then, the mixture was compounded using a biaxial kneader (same direction, TEM 35 made by Toshiba Kikai). Kunipia® F was contained in the produced composite material in an amount of 4 wt%. Its transparency was visually observed by an optical microscope and it was photographed (Figure 3).

20

Application Example 5

The same process used in Application Example 1 was used to make a Kunipia® F/poly(ethylene-methacrylic acid) potassium salt powder composite material (weight ratio = 1/3) (160 g). The material was dry-blended with pellets of poly(ethylene-methacrylic acid) zinc salt (Himilan® 1706 made by Du Pont-Mitsui Polychemicals Co., Ltd.) (840 g); then, the mixture was compounded using a biaxial kneader (same direction, TEM 35 made by Toshiba Kikai). Kunipia® F was contained in the produced composite material in an amount of 4 wt%. Its transparency was visually observed by an optical microscope and it was photographed (Figure 4).

30

Application Example 6

The same process used in Application Example 1 was used to make a Smecton® SA/poly(ethylene-methacrylic acid) potassium salt powder composite material (weight ratio = 1/1) (80 g). The material was dry-blended with pellets of poly(ethylene-methacrylic acid) zinc salt (Himilan® 1706 made by Du Pont-Mitsui Polychemicals Co., Ltd.) (840 g); then, the mixture was compounded using a biaxial kneader (same direction, TEM 35 made by Toshiba Kikai). Kunipia® F was contained in the produced composite material in an amount of 4 wt%. Its transparency was visually observed by an optical microscope and it was photographed (Figure 5). Transmission electromicrographs were taken (Figure 6).

Comparative Example 5

Kunipia® F (40 g) was made. It was dry-blended with pellets of polyethylene-methacrylic acid zinc salt (Himilan® 1707 made by Du Pont-Mitsui Polychemicals Co., Ltd.) (960 g); then, the mixture was compounded using a biaxial kneader (same direction, TEM 35 made by Toshiba Kikai). Kunipia® F was contained in the produced composite material in an amount of 4 wt%. Its transparency was visually observed by an optical microscope and it was photographed (Figure 7).

Optical microscopic photograph and electronmicrographs

As seen in both optical microscopic photographs and electromicrographs, in the case of dispersing layered silicate alone in poly(ethylene-methacrylic acid) zinc salt, large lumps were observed, and poor transparency was obtained. In the case of dispersing a layered silicate/poly(ethylene-methacrylic acid) potassium salt composite material in poly(ethylene-methacrylic acid) zinc salt, no large lumps were observed and good transparency was obtained. Layered silicate is dispersed better using a Kunipia® F/poly(ethylene-methacrylic acid) potassium salt powder composite material with a weight ratio equal to 1/3 in a final composite material than using a Kunipia® F/poly(ethylene-methacrylic acid) potassium salt powder composite material with a weight ratio equal to 1/1.

Application Example 7

The same process used in Application Example 3 was used to make a Kunipia® F/poly(ethylene-methacrylic acid) potassium salt powder composite material (weight ratio = 1/3) (16 g). The material was dry-blended with pellets of
5 poly(ethylene-methacrylic acid) zinc salt (Himilan® 1707 made by Du Pont-Mitsui Polychemicals Co., Ltd.) (84 g); then, the mixture was compounded using a biaxial kneader (same direction, TEM 35 made by Toshiba Kikai). Kunipia® F was contained in the produced composite material in an amount of 4 wt%. Its transparency was visually observed by an optical microscope and it was
10 photographed (Figure 8).

Comparative Example 6

Kunipia F (4 g) was made. It was dry-blended with pellets of poly(ethylene-methacrylic acid) zinc salt (Himilan® 1707 made by Du
15 Pont-Mitsui Polychemicals Co., Ltd.) (96 g); then, the mixture was compounded using a biaxial kneader (same direction, TEM 35 made by Toshiba Kikai). Kunipia® F was contained in the produced composite material in an amount of 4 wt%. Its transparency was visually observed by an optical microscope and it was
20 photographed (Figure 9).

Electromicrograph

As seen in the electromicrographs, in the case of dispersing layered silicate alone in poly(ethylene-methacrylic acid) zinc salt, large lumps were observed, and poor transparency resulted. In the case of dispersing layered
25 silicate/poly(ethylene-methacrylic acid) sodium salt composite material in poly(ethylene-methacrylic acid) zinc salt, no large lumps were observed, and good transparency resulted.

Effect of the invention

Layered silicate can be added to a polymer by an easy production method while maintaining transparency, if the polymer satisfies specific conditions, such as ionomer content. The reason for this is that the distance between the silicate
5 layers is increased and the polymer is introduced so that the silicate layers can be well dispersed in the polymer.

Claims

1. Production of a composite material, characterized by dispersing, mixing, drying, and crushing a polar organic polymer material that is either soluble or dispersible in water and fusible with silicate layers in a polar solvent to introduce the polar organic polymer to a layered silicate of the silicate layers.
2. Production of a composite material described in Claim 1, characterized by using an ionomer as the polar organic polymer.
3. Production of a composite material, characterized by dispersing, mixing, drying, and crushing 100 parts by weight potassium ionomer in which ethylene methacrylate copolymer is either partially or entirely neutralized with potassium, with 0.5-300 parts by weight silicate layers in water to introduce the potassium ionomer to a layered silicate of the silicate layers.
4. Production of a composite material, characterized by dispersing, mixing, drying, and crushing 100 parts by weight sodium ionomer which ethylene methacrylate copolymer is either partially or entirely neutralized with sodium and that can be soluble or dispersible in water, with 0.5-300 parts by weight silicate layers in water to introduce sodium ionomer to a layered silicate of the silicate layers.
5. A composite material characterized by containing both a polar organic polymer that is either soluble or dispersible in water and fusible, and that is introduced between the silicate layers.
6. Production of a composite-material-containing resin composition, characterized by compounding all of a composite material made by a production method described in any of Claims 1-4, a composite material described in Claim 5, and an organic polymer material compatible with the polar organic polymer to disperse and pack at least 0.05 part by weight of the silicate layers in 100 parts by weight of a mixture of the polar organic polymer and the organic polymer material.
7. A composite-material-containing resin composition characterized by containing a melted and kneaded material comprising composite material made by one of the production methods described in Claims 1-4, or composite material described in Claim 5, and an organic polymer material compatible with the polar

organic polymer, and by containing both the polar organic polymer, and at least 0.05 parts by weight of the above-mentioned silicate layers to 100 parts by weight of the above-mentioned organic polymer material.

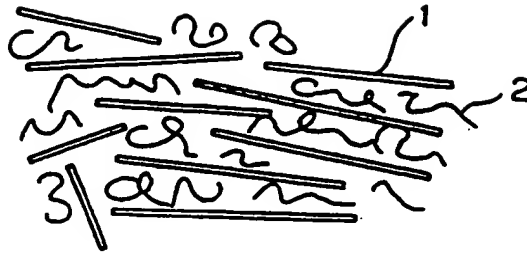


FIG. 1



FIG. 2

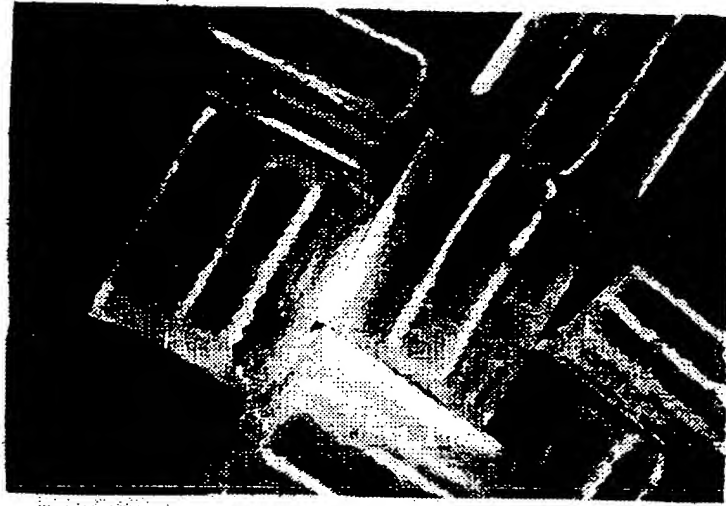


FIG. 3A



FIG. 3B

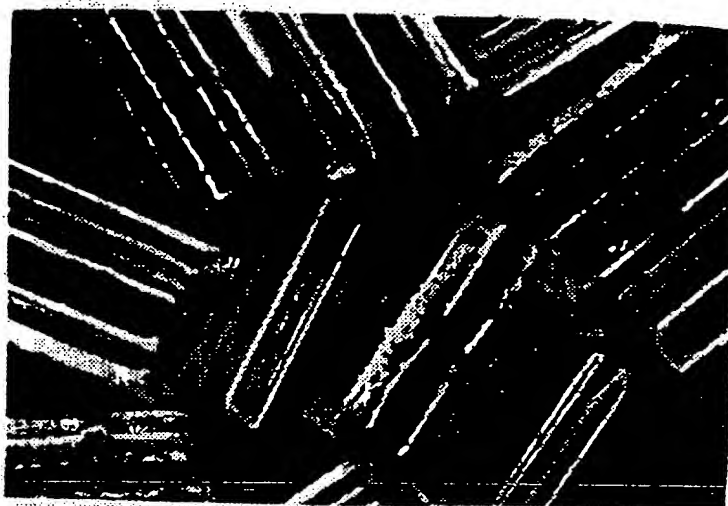


FIG. 4A

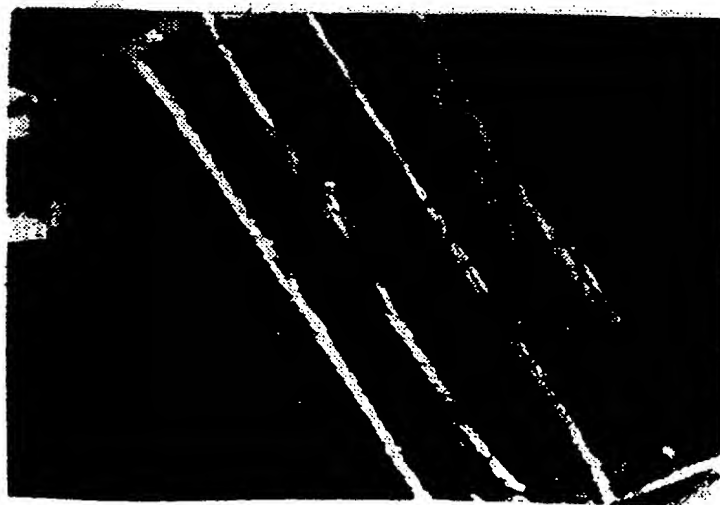


FIG. 4B



FIG. 5A



FIG. 5B

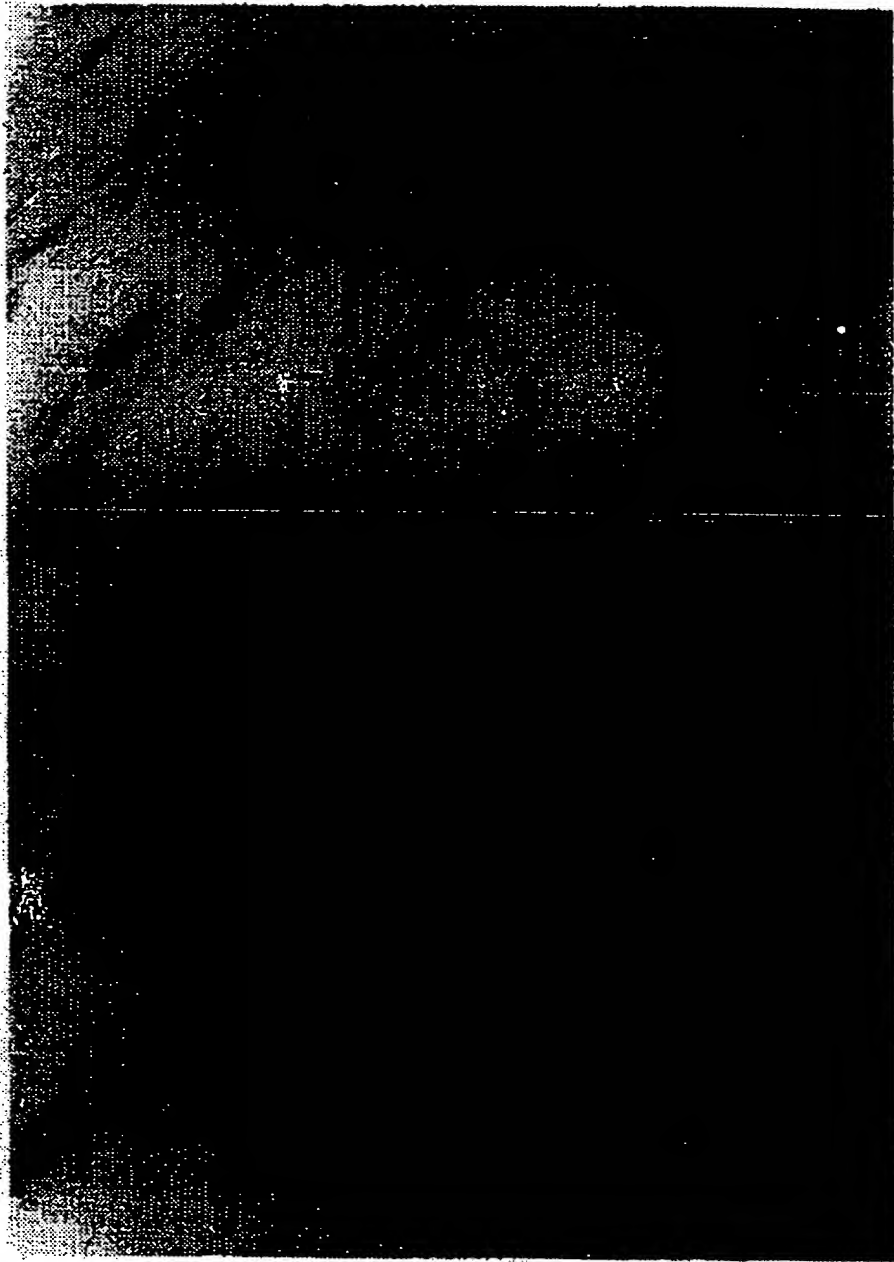


FIG. 6

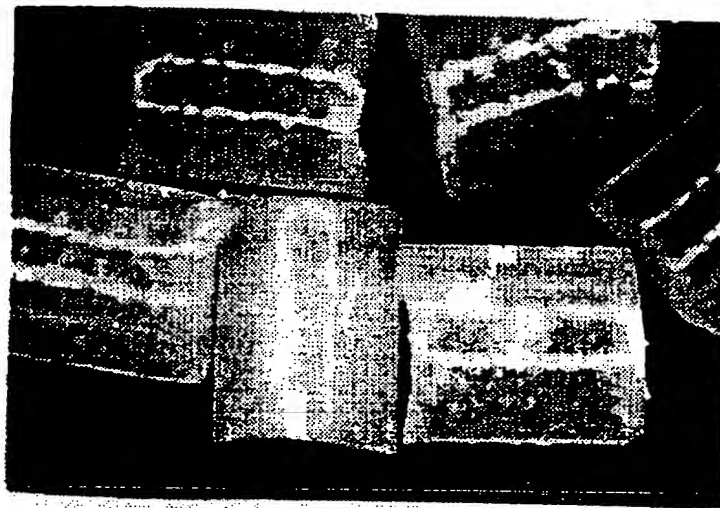


FIG. 7A

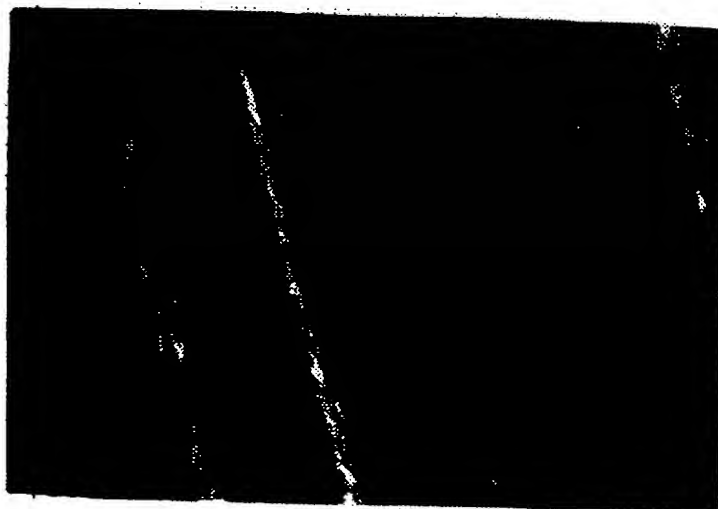


FIG. 7B

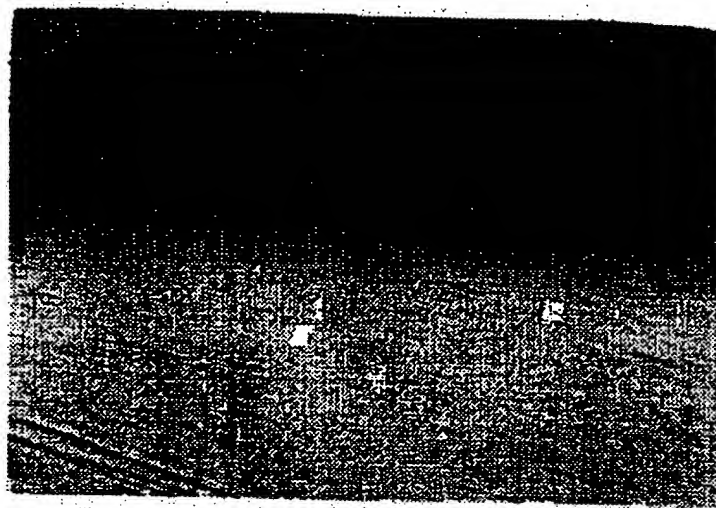


FIG. 8

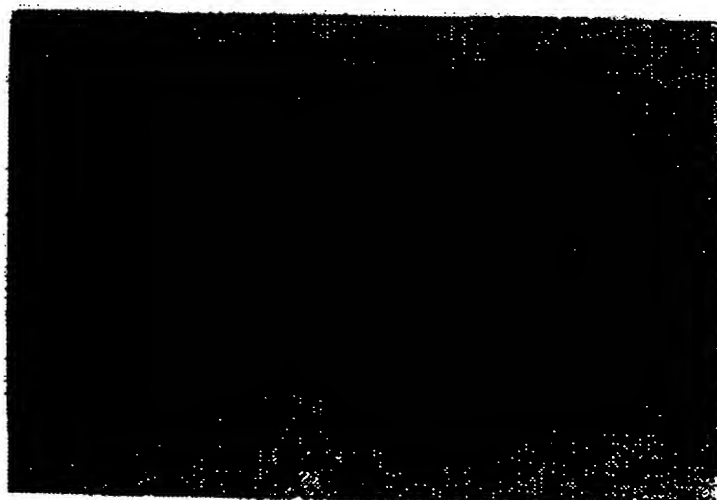


FIG. 9

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US97/03061

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C08K 3/34, 11/00 US CL : 524/442, 443, 4444, 445, 446, 447 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 524/442, 443, 4444, 445, 446, 447 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) APS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,385,776 (MAXFIELD ET AL) 31 January 1995 entire document.	1-2, 5-7
Y	US, A, 4,889,885 (USUKI ET AL) 26 December 1989 entire document.	1-2, 5-7
Y	US, A, 5,164,460 (YANO ET AL.) 17 November 1992 entire document.	1-2, 5-7
Y	us, a, 4,739,007 (OKADA ET. AL.) 19 April 1988 entire document.	1-2, 5-7
Y	US, A, 4,105,709 (IWAMI ET AL.) 08 August 1978 entire document.	3,4
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 12 JUNE 1997		Date of mailing of the international search report 07 AUG 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer U.K. RAJGURU Telephone No. (703) 305-2351

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